Diabolical Points in Magnetic Molecules: An Exactly Solvable Model

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Abstract

The magnetic molecule Fe_8 has been observed to have a rich pattern of degeneracies in its magnetic spectrum as the static magnetic field applied to the molecule is varied. The points of degeneracy, or diabolical points in the magnetic field space, are found exactly in the simplest model Hamiltonian for this molecule. The points are shown to form a perfect centered rectangular lattice, and are shown to be multiply diabolical in general. The multiplicity is found. An earlier semiclassical solution to this problem is thereby shown to be exact in leading order in $1/J$ where J is the spin.

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A famous theorem of quantum mechanics states that the intersection of two energy levels of a physical system is infinitely unlikely as a single parameter is varied [1]. Instead, level repulsion is the rule, and level crossing happens only when there is some symmetry. If one can vary more than one parameter, however (at least two if the Hamiltonian is real, three if it is complex), then degeneracies can be found at isolated points in the parameter space [2–6]. Such degeneracies are usually called "accidental", for as a rule the points obey no discernible pattern. Berry and Wilkinson's coinage for such degeneracies, "diabolical," emphasizes the same point, although the term originates less in any desire to attribute the phenomenon to a Mephistophelean hand, than in the fact that the energy surface near the degeneracy is a double cone, like an Italian toy called the *diavolo*. When exceptions occur, and the pattern of diabolical points or degeneracies is not random, as in the Kepler problem, or in the isotropic harmonic oscillator, one seeks (and sometimes finds) a higher dynamical symmetry of the Hamiltonian.

It is therefore of some interest that a whole array of diabolical points has been discovered by Wernsdorfer and Sessoli (WS) [7] in the magnetic spectrum of the molecular solid $[(\mathrm{tacn})_6\mathrm{Fe}_8\mathrm{O}_2(\mathrm{OH})_{12}]^{8+}$ (shortened to Fe_8 from now on). Strong intramolecular exchange interactions among the Fe^{3+} ions lead to a total spin of $J = 10$ in the ground manifold for each molecule, which can therefore be conceived of as a single large spin of this magnitude. The dipolar interactions between molecules are weak, and may be ignored. Spin-orbit interactions lead to an easy-axis anisotropy, with further differentiation in the non-easy plane. The simplest anisotropy Hamiltonian that describes the magnetic properties of one molecule is

$$\mathcal{H} = -k_2 J_z^2 + (k_1 - k_2) J_x^2 - g\mu_B \mathbf{J} \cdot \mathbf{H}, \tag{1}$$

with $k_1 > k_2 > 0$ ($k_1 \approx 0.33$ K, and $k_2 \approx 0.22$ K [8]), $g = 2$, and $\mathbf{H}$ is an external magnetic field. With Eq. (1), the easy, medium, and hard axes are $\hat{\mathbf{z}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{x}}$, respectively.

To understand the evidence for diabolicity, let us suppose that the field $\mathbf{H}$ is along the hard axis, $\hat{\mathbf{x}}$, and not too large. The easy directions, which are along $\pm\hat{\mathbf{z}}$ when $\mathbf{H} = 0$, cant symmetrically toward $\hat{\mathbf{x}}$. At first sight, as H_x is increased, it should be progressively easier for the spin to tunnel from a state localized in the potential well in the positive J_z hemisphere to the symmetrically located state in the negative hemisphere. It was found some time ago, however, that in the model (1), the tunnel splitting between the ground states in the positive and negative J_z wells actually oscillates as a function of H_x, going to zero at periodically spaced H_x values [9]. Precisely these oscillations have been seen by WS in Fe_8. The oscillations were initially explained [9] in terms of an interference between instanton trajectories for the spin, and the observations on Fe_8 are very hard to explain by other mechanisms. The clincher is that WS see additional oscillations that were not predicted. To understand these, suppose $\mathbf{H}$ also has a nonzero z component so as to bring the first or second excited state in the positive J_z well into degeneracy with the ground state in the other well. One can then conceive of tunneling between these states. WS observe that the amplitude for this tunneling also oscillates with H_x, and that the oscillations are shifted by half a period for each excited state in the deeper well.

That the tunnel splitting between two states vanishes, is merely another way of saying that the states are exactly degenerate. The degeneracies that lie on the H_x or H_z axes in the magnetic field space can be understood in terms of symmetry allowed level crossings as

per the von Neumann-Wigner theorem [10], but the newly discovered ones by WS lie off the axes, and cannot be so understood. They are truly nontrivial instances of diabolical points. Since the experiments were reported, they have been successfully explained by one of us (AG) [11], and independently, Villain and Fort [12]. The approach is based on a discrete version of the phase integral or Wentzel-Kramers-Brillouin method, and is semiclassical in nature, with $1/J$ playing the role of $\hbar$ in continuum problems with massive particles. It is found that the ℓ'th level in the negative J_z well (with $\ell' = 0$ being the lowest level) and the ℓ''th level in the positive one are degenerate when $H_y = 0$, and (see Fig. 1)

$$\frac{H_z(\ell', \ell'')}{H_c} = \frac{\sqrt{\lambda}(\ell'' - \ell')}{2J} \tag{2}$$

$$\frac{H_x(\ell', \ell'')}{H_c} = \frac{\sqrt{1-\lambda}}{J}\left[J - n - \tfrac{1}{2}(\ell' + \ell'' + 1)\right], \tag{3}$$

with $n = 0, 1, \ldots, 2J - (\ell' + \ell'' + 1)$. Here, $\lambda = k_2/k_1$, and $H_c = 2k_1 J/g\mu_B$. Note that these equations do give a half-period shift per excited state, as seen by WS.

The surprise is that although Eqs. (2) and (3) are dervied semiclassically, and should have higher order corrections in $1/J$, they appear to be exact as written! This has been noted by both Villain and Fort, and AG. The evidence is from (a) analytic diagonalization for $J \leq 2$, (b) perturbation theory in λ [13], and (c) numerics. Note that if exact, Eqs. (2) and (3) would imply not only that the diabolical points lie on a perfect centered rectangular lattice in the H_x-H_z plane, but also that many of the points are *multiply* diabolical, i.e., that more than one pair of levels is simultaneously degenerate. It is easily shown that the multiplicity is as indicated in Fig. 1: If we arrange the points into concentric rhombi, those on the outermost rhombus are singly diabolical (i.e., there is only one pair of degenerate states), those on the next rhombus are doubly diabolical (two pairs of degenerate states), and so on.

In this paper we shall prove that this perfect lattice hypothesis is in fact true. Not only is this an interesting problem in mathematical physics in its own right, but we believe that it will help understand real Fe_8 also. Exact solutions generally open the way for perturbative treatment of small corrections, and in Fe_8, we beleive our work will enable us to better treat such effects as the higher order anisotropies and the dipolar interactions mentioned above, and allow more detailed understanding of nonzero temperature effects [14].

Before giving our proof, we should note that we have not been able to find if the Hamiltonian (1) has a higher symmetry at the diabolical points. Such a suspicion is natural, given the experience with the exceptional cases mentioned in our first paragraph. Likewise, we have not succeeded in finding the wavefunctions. We also note that the semiclassical approximation is demonstrably inexact at non diabolical values of $\mathbf{H}$, in order to dispel any suspicion in the readers' minds that the classical and quantum dynamics of the Hamiltonian (1) are identical as in the case of the harmonic oscillator.

We now present our proof. It proceeds in three steps. In step 1 we perform a spin rotation about $\hat{\mathbf{y}}$ so that $\mathcal{H}$ no longer has any terms in J_x^2. The Hamiltonian is then tridiagonal in the new J_z basis. In step 2 we make use of a necessary condition for a tridiagonal Hermitean matrix to have degenerate eigenvalues, and thus determine the possible locations of any diabolical points. In step 3, we use continuity and topological arguments to find the multiplicity of each of these diabolical points. The results are precisely those given above.

Step 1: Let us rotate $\mathbf{J}$ about the $\hat{\mathbf{y}}$ axis so that

$$\begin{pmatrix} J_z \\ J_x \end{pmatrix} \to \begin{pmatrix} \sqrt{\lambda} & \sqrt{\bar{\lambda}} \\ -\sqrt{\bar{\lambda}} & \sqrt{\lambda} \end{pmatrix} \begin{pmatrix} J_z \\ J_x \end{pmatrix}, \tag{4}$$

where $\bar{\lambda} = 1 - \lambda$. It is also convenient to define scaled fields u_x, u_y, and u_z via

$$\mathbf{H} = \frac{H_c}{2J}(\sqrt{\bar{\lambda}}u_x,\ u_y,\ \sqrt{\lambda}u_z), \tag{5}$$

to scale all energies by k_1, and to write $\overline{\mathcal{H}} = \mathcal{H}/k_1$. In the new axes, we have

$$\begin{aligned} \overline{\mathcal{H}} = &-(\lambda - \bar{\lambda})J_z^2 - \sqrt{\lambda\bar{\lambda}}(J_zJ_x + J_xJ_z) \\ &- \left[(\lambda u_z - \bar{\lambda}u_x)J_z + \sqrt{\lambda\bar{\lambda}}(u_x + u_z)J_x + u_yJ_y\right]. \end{aligned} \tag{6}$$

Step 2: The Hamiltonian (6) is tridiagonal in the the new J_z basis, $J_z|m\rangle = m|m\rangle$. Its only nonzero matrix elements are $\langle m|\overline{\mathcal{H}}|m\rangle \equiv w_m$, and $\langle m|\overline{\mathcal{H}}|m'\rangle \equiv t_{m,m'}$, with $m' = m \pm 1$. And, it is obviously Hermitean: $w_m^* = w_m$, $t_{m,m'} = t_{m',m}^*$. For such matrices, it is a theorem that all the eigenvalues are simple (i.e., nondegenerate) if none of the $t_{m,m'}$ vanish [15]. This result is physically almost obvious if one thinks of $\overline{\mathcal{H}}$ as a tight-binding model for an electron in one dimension with on-site energies w_m and nearest neighbor hopping elements $t_{m,m\pm1}$. Two states which were degenerate could be spatially localized in different regions of the lattice. But then, since $t_{m,m\pm1} \neq 0$ for any m, it would be possible for the electron to hop from one region to the other, which is self-contradictory. The rigorous proof by Stoer and Bulirsch consists of noting that the successive diagonal subdeterminants of $\overline{\mathcal{H}} - EI$ (where I is the unit matrix), form a Sturmian sequence of polynomials $p_j(E)$, $j = 1, 2, \ldots, 2J+1$, with the properties that p_j is of degree j, has j real roots, each one of which is simple, and is strictly bracketed by two roots of p_{j+1}.

It follows that the diabolical points of $\overline{\mathcal{H}}$, if any, must lie on the loci in magnetic field space defined by $t_{m,m+1} = 0$. Using the standard representation of the angular momentum matrices, we have

$$t_{m,m+1} = -\frac{1}{2}\left[(u_x + u_z + (2m+1))\sqrt{\lambda\bar{\lambda}} + iu_y\right][J(J+1) - m(m+1)]^{1/2}. \tag{7}$$

The real and imaginary parts of this quantity must vanish separately for some m. We thus conclude that any diabolical points must lie in the H_x-H_z plane:

$$u_y = 0, \tag{8}$$

and in this plane on the lines

$$u_x + u_z = -(2m_0 + 1), \quad m_0 = -J, -J+1, \ldots, J-1. \tag{9}$$

Further, when these conditions are obeyed, $\overline{\mathcal{H}}$ divides into two blocks, of size n_n and n_p, with $n_n = J + m_0 + 1$, and $n_p = J - m_0$. In the first block, $m \leq m_0$, and in the second $m \geq m_0 + 1$.

The conditions (8) and (9) are not enough to locate the diabolical points. However, we can repeat our argument, starting with a rotation (4) in which the signs of the $\sqrt{\lambda}$ entries are reversed. In this way we find that at a diabolical point, we must also obey the condition

$$u_x - u_z = -(2n_0 + 1), \quad n_0 = -J, -J+1, \ldots, J-1, \tag{10}$$

which along with Eq. (9) fixes the points completely. Solving these equations, we get

$$\begin{aligned} u_x &= -(m_0 + n_0 + 1), \\ u_z &= n_0 - m_0, \end{aligned} \tag{11}$$

which with Eq. (5) are identical to Eqs. (2) and (3).

Step 3: It remains to find just how many pairs of levels are degenerate at each of the points (11). To do this, we first show that under a continuous change in the parameter λ, the diabolical points of the Hamiltonian (1) must evolve smoothly in the u_x-u_z plane. In particular, the number of diabolical points must stay fixed. We present two arguments for this, one more physical, and the other more mathematical.

The physical argument is much like the standard one [2] for the von Neumann-Wigner theorem. Suppose that for some $\lambda = \lambda_0$, $\overline{\mathcal{H}}$ has two degenerate states $|\psi_a\rangle$ and $|\psi_b\rangle$ at $u_x = u_{x0}$, $u_z = u_{z0}$. (We set $u_y = 0$ throughout.) Now let λ be changed by a small amount $\delta\lambda$. We seek new eigenstates in the first approximation as linear combinations of $|\psi_a\rangle$ and $|\psi_b\rangle$. The secular matrix in this subspace is given by

$$\begin{pmatrix} \overline{\mathcal{H}}_{aa} & \overline{\mathcal{H}}_{ab} \\ \overline{\mathcal{H}}_{ba} & \overline{\mathcal{H}}_{bb} \end{pmatrix}, \tag{12}$$

with $\overline{\mathcal{H}}_{ba} = \overline{\mathcal{H}}_{ab}$ since with $u_y = 0$, the Hamiltonian is real. Here, $\overline{\mathcal{H}}_{aa}$, $\overline{\mathcal{H}}_{ab}$, etc., are all smooth functions of λ, u_x, and u_z. The eigenvalues of this matrix will be equal if and only if $\overline{\mathcal{H}}_{aa} = \overline{\mathcal{H}}_{bb}$, and $\overline{\mathcal{H}}_{ab} = 0$. Expanding these conditions in the deviations from λ_0, u_{x0}, and u_{z0}, we get

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} \delta u_x \\ \delta u_z \end{pmatrix} = \delta\lambda \begin{pmatrix} e \\ f \end{pmatrix}, \tag{13}$$

where the quantities a through d are partial derivatives of $\overline{\mathcal{H}}_{aa}$ etc. with respect to u_x and u_z, and e and f are partial derivatives with respect to λ. Since the diabolical point for $\lambda = \lambda_0$ is isolated, it follows that the only solution to Eq. (13) when $\delta\lambda = 0$ is $\delta u_x = \delta u_z = 0$, i.e., that the matrix on the left hand side is nonsingular, and a nonzero solution can be found when $\delta\lambda \neq 0$. It follows in turn that the diabolical point can only be moved, and not eliminated or created by changing λ.

The second argument is based on Berry's phase [16]. Let us consider a diabolical point as in the preceding paragraph, and let C be a small closed contour in the u_x-u_z plane encircling this point. Berry's phase is given by

$$\gamma(C) = i \oint_C \langle \psi_a(\lambda, \mathbf{u}) | \nabla_{\mathbf{u}} \psi_a(\lambda, \mathbf{u}) \rangle \cdot d\mathbf{u}, \tag{14}$$

where $\mathbf{u} = (u_x, u_z)$, and $\nabla_{\mathbf{u}}$ is a gradient with respect to these fields. As shown by Berry, $\gamma(C) = \pm\pi$ if C encloses a true diabolical point, and $\gamma(C) = 0$ if the two states merely

approach each other very closely without ever being degenerate. [Actually, since our Hamiltonian is real, and the parameter space (u_x, u_z) is two-dimensional, we really only need the weaker result due to Herzberg and Longuet-Higgins [3] for the sign change of the wavefunction upon encircling the degeneracy: $e^{i\gamma(C)} = -1$.] Since the perturbation $\delta\overline{\mathcal{H}}$ engendered by changing λ or $\mathbf{u}$ by a small amount is non-singular, $|\psi_a(\lambda, \mathbf{u})\rangle$ is a smooth function of λ and $\mathbf{u}$. It follows that if λ varies continuously, the integrand of Eq. (14) can not change discontinuously. Hence, for small enough $\delta\lambda$, the phase $\gamma(C)$ must continue to be what it was for $\lambda = \lambda_0, +\pi$, say, implying that C continues to encircle a degeneracy.

The rest is plain sailing. Consider $\overline{\mathcal{H}}$ in the form (6), and let u_x and u_z be one of the points (11). As noted before, $\overline{\mathcal{H}}$ divides into two blocks at this point. Consider now how the eigenvalues of each block change as λ is varied. Suppose the variation is as depicted in Fig. 2. This would imply that the total diabolicity of our system changes discontinuosly, in violation of the result just proved. Thus a behavior as in Fig. 2 is impossible, and the correct picture is as in Fig. 3. One can also see that the behavior can not be that as in Fig. 2 for some (m_0, n_0) and that as in Fig. 3 for others, since there is then no way to keep the total diabolicity constant.

We thus conclude that the multiplicity $f(m_0, n_0)$ of the diabolical point at (m_0, n_0) is independent of λ, and we may find it by evaluating it for any one value of λ. We do this for $\lambda = 0$, as $\overline{\mathcal{H}}$ is then not just tridiagonal, but diagonal. Degeneracy occurs whenever

$$w_{m_1} = w_{m_2}, \quad (m_1 \leq m_0; \quad m_2 \geq m_0 + 1). \tag{15}$$

Since $w_m = m^2 - (m_0 - n_0)m$ for $\lambda = 0$, this condition becomes

$$m_1 + m_2 = m_0 - n_0. \tag{16}$$

The problem is now one of counting. We leave it as an exercise to show that with the conditions in Eq. (15) on m_1 and m_2, and in Eqs. (9) and (10) on m_0 and n_0, the number of solutions to Eq. (16) is given by

$$f(m_0, n_0) = \frac{1}{2}[2J + 1 - |m_0 - n_0| - |m_0 + n_0 + 1|]. \tag{17}$$

This is precisely the multiplicity implied by Eqs. (2) and (3). One way to see this is to evaluate f on the rhombi drawn in Fig. 1, in particular, the segment lying in the first quadrant in the H_x-H_z plane. Regarding the outermost rhombus as the first, the next as the second, etc., we have $m_0 = -(J + 1) + k$ on the kth one. Further, for the part in the first quadrant, n_0 ranges from m_0 to $J - k$. Thus $(m_0 - n_0)$ and $(m_0 + n_0 + 1)$ are both negative, and

$$\begin{aligned} f(m_0, n_0) &= \frac{1}{2}[2J + 1 + (m_0 - n_0) + (m_0 + n_0 + 1)] \\ &= J + m_0 + 1 \\ &= k, \end{aligned} \tag{18}$$

exactly as expected.

For completenes, we conclude by observing that our results obey the symmetries of the Hamiltonian. First, for half-integral J, the point at $\mathbf{H} = 0$ corresponds to $m_0 = n_0 = -1/2$.

The value of f is then $J + \frac{1}{2}$, i.e., every state is doubly degenerate, as required by Kramers' theorem. Second, the reflection symmetries $H_x \to -H_x$, $H_z \to -H_z$ are clearly obeyed by the set (2) and (3). In terms of the quantities m_0 and n_0, these symmetries correspond to $m_0 \to -(m_0 + 1)$ and $n_0 \to -(n_0 + 1)$, and it is easy to see from Eq. (17) that these leave f unchanged. Lastly, the Hamiltonian (1) has the following *duality* property. Showing its dependence on λ, H_x and H_z explicitly by writing $\mathcal{H}(\lambda, H_x, H_z)$, we note that a 90° rotation about $(\hat{\mathbf{x}} + \hat{\mathbf{z}})/\sqrt{\mathbf{2}}$ yields the transformation

$$\mathcal{H}(\lambda, H_x, H_z) \leftrightarrow -\mathcal{H}(1 - \lambda, H_z, H_x). \tag{19}$$

In particular, the spectra of the two Hamiltonians are so related, and ranking the levels is order of increasing energy, we see that if the levels with ordinal numbers i and $i + 1$ are degenerate when $H_x = f_x(\lambda)$ and $H_y = f_y(\lambda)$, where the functions f_x and f_y are unknown, then level numbers $2J + 2 - i$ and $2J + 1 - i$ are degenerate when $H_x = f_y(1 - \lambda)$ and $H_y = f_x(1 - \lambda)$. This property is also obeyed by Eqs. (2) and (3), and (17).

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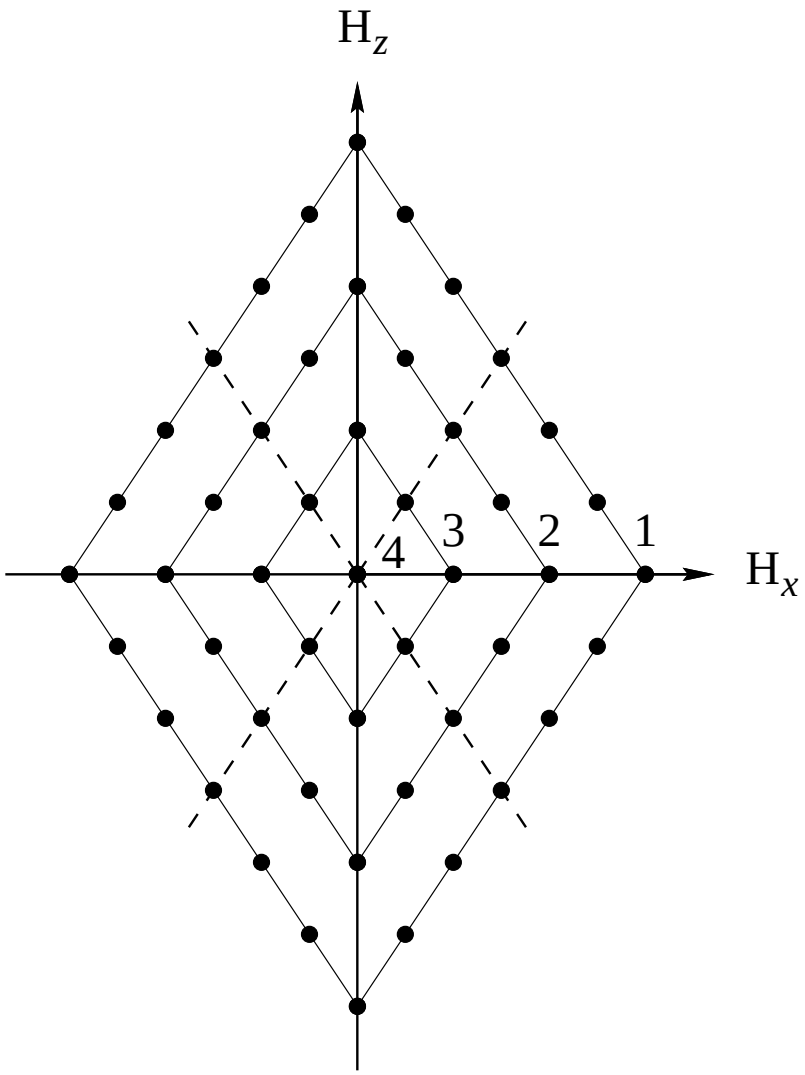
FIGURES

FIG. 1. Diabolical points for the model Hamiltonian (1), shown for the case $J = 7/2$. The points can be organized into rhombi (including the degenerate central rhombus with only one point). All points on a rhombus have the same multiplicity, i.e., number of simultaneously degenerate levels. These numbers are as shown. The dashed lines are self-dual under the transformation (19).

FIG. 2. Impermissible variation of the energy levels with λ for fixed m_0 and n_0. The solid curves are the energies of one of the blocks of $\overline{\mathcal{H}}$, and the dashed curves of the other.

FIG. 3. Same as Fig. 2, except that the variation is now permissible. The solid and dashed curves drawn right next to each other are in fact coincident.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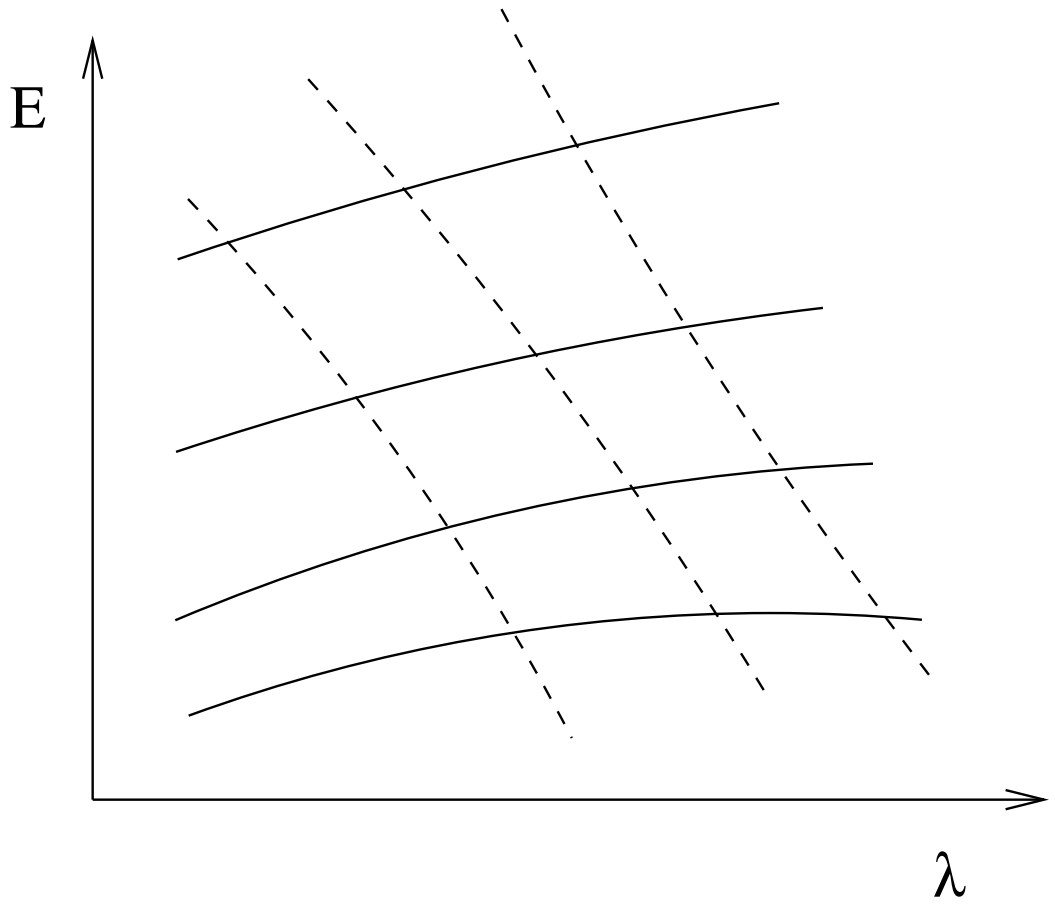
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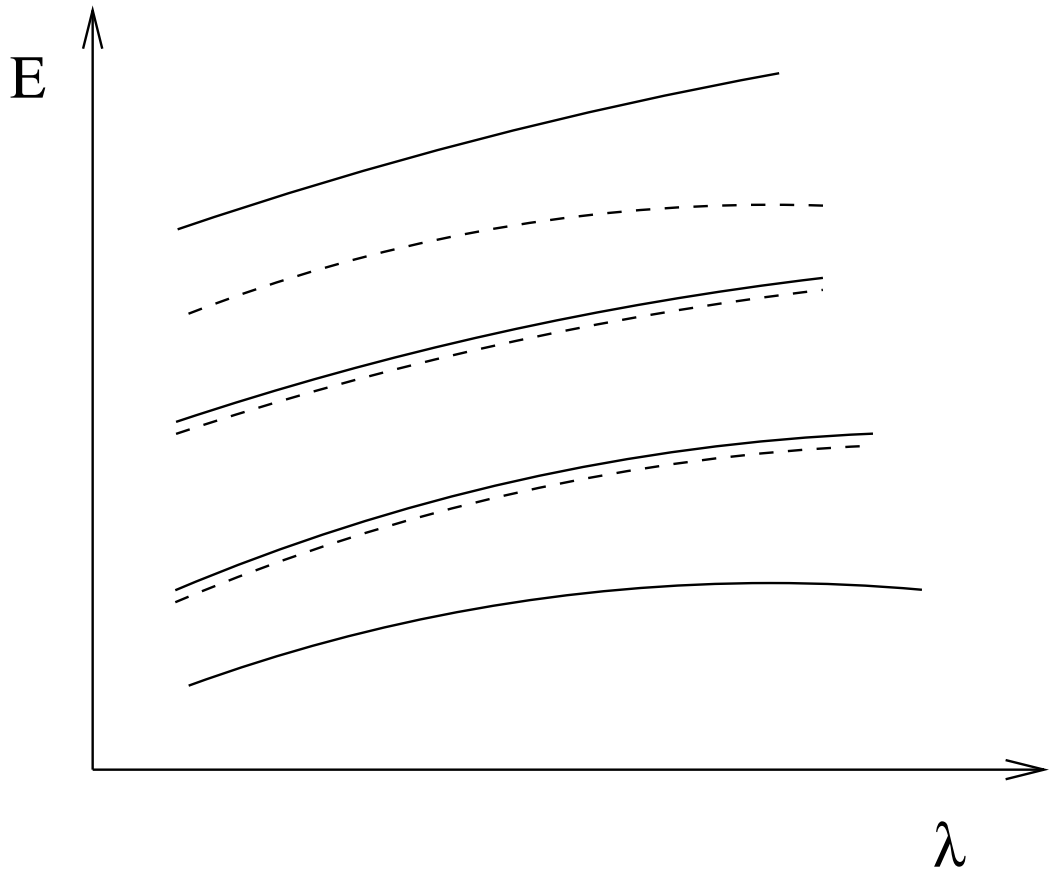
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